Emulsion Liquid Membrane for Copper and Cadmium Removal in Taylor-Couette Column

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***Abstract*— In this study, Emulsion Liquid Membrane (ELM) was for copper and cadmium removal in Taylor-Couette Column (TCC). ELM is a double emulsion of water/oil/water (W/O/W) system consists of three main phases which are membrane phase, internal phase and external phase, while TCC was used to obtain a better mixing condition with a uniform and relatively low fluid shear to maintain the emulsion stability. The chemicals used in this study are Bis(2-ethylhexyl) phosphate (D2EHPA) as carrier, Span 80 as surfactant, kerosene as diluent and hydrochloric acid (HCl) as internal phase. Meanwhile, copper nitrate ($Cu(NO_3)_2$) and cadmium nitrate ($Cd(NO_3)_2$) solution were used as the external phase. The extraction of copper was executed in a counter rotating TCC and samples were analyzed using Atomic Absorption Spectrophotometer (AAS) to determine the copper and cadmium concentration in external phase. This research was done to study the mixing of water-oil-water (W/O/W) emulsions in Taylor-Couette flow and to identify the best condition to achieve high copper and cadmium removal using ELM in TCC. The parameters involved are the external phase pH, extraction time and rotational speed of the TCC outer cylinder. It was found that pH 4 was the most optimum pH to achieve the maximum extraction efficiency of copper (92.72%) and cadmium (81.29%). While the highest efficiency for copper was at stirring speed of 200 rpm in 5 minutes (96.38%) and cadmium at 600 rpm in 3 minutes (81.59%).**

Keywords*— *Emulsion liquid membrane, heavy metal extraction, Taylor-Couette Column, extraction efficiency.

I. INTRODUCTION

Reducing hazardous metals content in liquid effluent streams has already been a general discussion nowadays. Virulent heavy metal ions commonly found in discharged industrial waste water has been of great concern to not only the environment, but also towards humans' health [1]. According to the World Health Organization, WHO [2], some of the metals with the greatest concern include copper, aluminum, arsenic and cadmium. Heavy metals are non-biodegradable in nature; hence they have the tendency to be accumulating in living creatures, which leads to several disorders and diseases [3]. Excessive accumulation of copper and cadmium may cause acute poisoning of copper which contributes to diarrhea, gastroenteritis, dehydration, anorexia and shock, while severe copper poisoning causes Wilson's, Menkes and Alzheimer's diseases [4]. Not only that, excessive exposure of cadmium to humans will cause headache, nausea, vomiting, depression, lethargy, kidney damage, renal disorder, asthma, cough and neurological disorder such as seizure, ataxia and unusual thirst [5]. Copper(II) ions are released in huge amounts into the open water in environment through the wastewater originated from various industries such as steelworks, metallurgy, mining, plating, petroleum refining, paper and pulp, wood preservatives, fertilizer and circuit printing [6]. Meanwhile, cadmium exists naturally as a minor constituents of base metal ores and coal deposits, and also exists as a toxic heavy metal found in industrial discharges of various industries such as manufacturing of cadmium, phosphate fertilizers, nickel batteries, stabilizers, pigments, alloys and electroplating industries which can harm the environment [7].

In the way to overcome the barrier towards a sustainable future with favorable environment, many methods are issued by researchers to extract heavy metals specifically copper and cadmium from waste water. The way to achieving the most perfect method however, is still too far with most of the methods proposed still need to be improved.

Emulsion liquid membrane (ELM) introduced by Li [8] was proposed as one of the promising techniques due to its potential as a highly efficient method for industrial aqueous effluent waste treatment. Instead of using a number of separate equipment, ELM that combines extraction and stripping process in one system not only able to purify, but also to concentrate the solute simultaneously which makes this system economically feasible [9]. Not only that, ELM extraction provides large interfacial area to volume ratio for mass transfer, consumes lower energy and is most efficient for low solute concentration or small quantity of solvent [10].

ELM system in double emulsions form might consists of two types: oil-water (O/W) emulsion dispersed in outer organic phase and water-oil (W/O) emulsion dispersed in external aqueous phase. The membrane phase in water-oil-water (W/O/W) type is immiscible oil phase separating the aqueous phase, while in the O/W/O type is immiscible water phase separating two organic phases that act as the membrane. Therefore, the liquid membrane provides a dual function of allowing selective transfer of one or more components through it from external phase to internal droplets and vice versa; and to prevent external and internal phases from getting mixed [11].

Technically, ELM process contains three main steps where the first step is to prepare the emulsion by mixing membrane phase and internal phase such as water-in-oil (W/O), where water is dispersed into the oil in the form of fine droplets or globules as depicted in Figure 2. The second step is solute permeation through membrane phase from an external phase to an internal phase by interfacial contact between emulsion and external phase containing metal waste. And for the last step, the emulsion and external phase are settling which is then continued by demulsification for the membrane phase recovery [12]. In general, the main components of ELM as shown in Figure 1, basically consist of carrier to promote the transfer of solute through membrane, surfactant to lower the interfacial tension between oil and water through adsorption at the liquid-liquid interface [11], diluent in which carrier is dissolved with any possible modifier to form a solvent [13], and lastly internal and external phase.

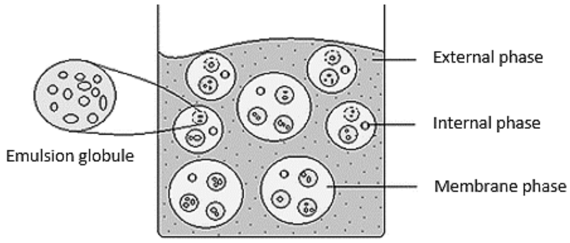

Figure 1: Main components of ELM [14]

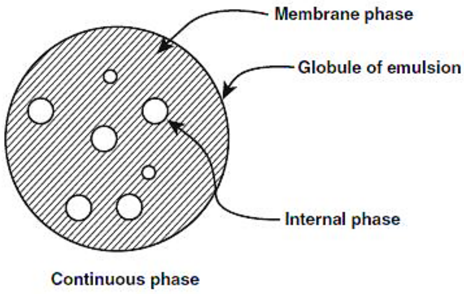

Figure 2: Emulsion liquid membrane droplet [15]

The principle of rate-determining step in solute permeation across a liquid membrane is the solute diffusion through membrane. Nevertheless, separation can be further improved through the addition of carriers, additives, chemical reagents, or external electric or photoelectric impulses. The wide variety of separation mechanisms are extensively discussed by many.

However, the effectiveness of the overall system of ELM is majorly threatened by the instability problem, mostly membrane breakage and emulsion swelling. Since the ELM tolerance for membrane breakage and emulsion swelling are about 0.1% and 10%, respectively [16], it is crucial to maintain the stability at its desired level for ELM to render applicable in industrial scale. The diameter of emulsion small droplet acts as the key criterion in providing stable emulsion and larger surface area for higher extraction efficiency. Despite its key role in the application of ELM, maintaining stability in the system however, is definitely not an easy task.

Hence, Taylor-Couette column (TCC) is proposed replacing the conventional stirrer as it can offer a better mixing condition with a uniform and relatively low fluid shear that is helpful in maintaining the emulsion stability without undermining the extraction efficiency [9, 16]. Study done by Ahmad, et al. [9] indicated that the most optimum concept is when the desired component is extracted in a counter rotating TCC where the inner cylinder rotates in constant speed and at the same time, the outer cylinder rotates in opposite direction at varying speed. This system offers high overall removal efficiencies as the outer cylinder speed increases in a relatively brief contact time. Nevertheless, common TCC with single inner cylinder rotation is found effective only in a narrow gap of the two cylinders for greater fluid mixing hence disrupt the working capacity [9]. Therefore, further study still needs to be done since the emergence of ELM with TCC is relatively new for the application of liquid membrane. In this paper, the study was done to investigate the mixing of water-oil-water (W/O/W) emulsion in Taylor Couette flow and to identify the best condition to achieve high copper and cadmium removal using ELM in TCC. In view of this, the current study investigates the effect of external phase pH, extraction time and rotational speed of the TCC outer cylinder on the copper and cadmium extraction efficiency utilizing emulsion liquid membrane in Taylor-Couette Column.

II. METHODOLOGY

A. *Materials*

Deionized water was used for all solutions preparations. The chemicals used to develop the ELM system and their purposes were listed in Table 1.

Table 1: List of chemicals used and their purposes

Chemicals	Brand	Purpose
Kerosene	Commercial grade	Diluent
Span 80	Merck	Surfactant
Bis(2-ethylhexyl) phosphate (D2EHPA)	Sigma Aldrich	Carrier
Hydrochloric acid (HCl)	Fischer	Internal phase
Copper (II) nitrate and Cadmium (II) nitrate	Systerm and Sigma Aldrich	External phase

B. *ELM preparation*

The membrane phase was prepared by dissolving Span 80 (surfactant) and D2EHPA (carrier) in kerosene (diluent) and stirred at 300 rpm for 5 minutes using magnetic stirrer [9]. After that, hydrochloric acid (HCl) as the internal phase was mixed into the membrane phase solution at volume ratio of membrane to internal phase of 3:1 [16]. The mixture was homogenized for 15 minutes at stirring speed of 8000 rpm using homogenizer (WITEG HG-15D). The probe was immersed at the interface of the membrane-internal phase which then produced water-oil (W/O) emulsion [17]. The emulsion was then used to extract solute from the external phase.

The process was further continued by dispersing the primary W/O emulsion into the external phase containing Copper (II) ions and Cadmium (II) ions. The external phase was prepared prior mixing with W/O emulsion by dissolving Copper (II) nitrate and Cadmium (II) nitrate both with equal amount of 50 ppm in acetate buffer media where the pH was adjusted and kept constant at pH 4. The mixing process of W/O emulsion in the external phase solution produced water-oil-water (W/O/W) emulsion.

C. *Copper and cadmium extraction*

The study for extraction process was executed in a Taylor-Couette column (TCC) as pictured in Figure 3 at varying operation conditions. The parameters investigated in this study includes external phase pH and rotational speed of outer cylinder as function of extraction time. The inner cylinder of TCC was rotated at low constant speed of 40 rpm while the outer cylinder is rotated in opposite direction at varying speed ranging from 0 to 600 rpm [16]. After extraction completed, the solution was let to settle down for 5 minutes to make sure the emulsion and external phase were completely separated due to the act of gravity, before sample was taken from the bottom of the column for analysis to test the final concentration of copper and cadmium ions.

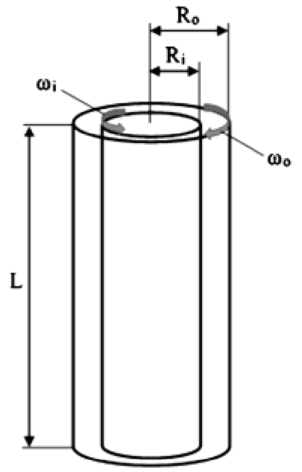

Figure 3: Schematic diagram of the counter-current rotating TCC cell used for heavy metal extraction (R_i = radius of inner cylinder; R_o = radius of outer cylinder; ω_i = angular velocity of inner cylinder; ω_o = angular velocity of outer cylinder; L = length of the column) [9].

D. Analytical procedure

The metal content in external phase was determined spectrophotometrically using Atomic Absorption Spectrophotometer model HITACHI Z-2000 at wavelength of 324.8 nm for copper and 228.8 nm for cadmium to determine the efficiency of extraction, Eff(%) [9]:

$$Eff(\%) = \frac{C_e^0 - C_e}{C_e^0} \times 100\% \quad (1)$$

where C_e^0 is the initial concentration of copper or cadmium in external phase (ppm), while C_e is final concentration of copper or cadmium in the solute (ppm).

III. RESULTS AND DISCUSSION

A. The effect of pH on extraction efficiency

A graph of pH versus extraction efficiency was plotted in Figure 4 where there was less significant difference of trends were shown between the copper and cadmium plots. The curve line for the plots was also in agreement with the graph pictured by Chakraborty, et al. [11] where the graph indicates that the initial efficiency decreases from pH 1 to 3 and started to drastically increases at pH 4, while experiencing significant downfall at pH 11.

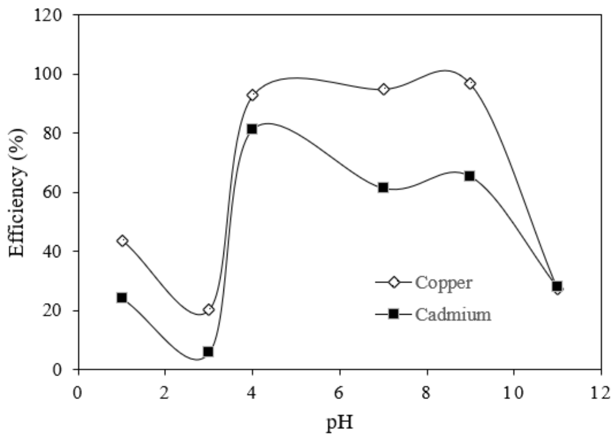

Figure 4: Effect of external phase pH on copper and cadmium extraction efficiency using TCC (surfactant concentration = 4 wt%; carrier concentration = 4 wt%; extraction time = 5 min; outer cylinder rotational speed = 600 rpm).

Figure 4 showed that the extraction efficiency went a significant downfall from pH 1 to 3, indicated that the initial copper and cadmium extraction rate were directly proportional to the hydrogen ion concentration in the external solution due to the existence of cadmium and copper as predominant anion only at low pH. While at higher pH, the cation species will mostly predominate. Therefore, the solute depletion was faster if the external phase was acidic [11, 18]. Based on Figure 4, the highest efficiency rate for cadmium was recorded at pH 4 where 81.29% of cadmium was extracted from the water, while on the other hand, pH 9 recorded the highest extraction efficiency for copper where 96.56% of copper was extracted. However, since pH 9 is alkaline, there was high possibility of metal precipitation resulted from the chemical reaction of copper nitrate with sodium hydroxide producing a precipitate of sodium nitrate. Hence, higher pH in alkaline will not be taken into consideration since the cupric hydroxide started to precipitate when the pH gets higher than 7.5 [19, 20].

In the investigated range, Cu(II) flux, permeability and removal efficiency increased as the external phase pH increased from 1 to 4. This result was expected since the driving force of the transport process is the gradient of the proton chemical potential (concentration) between the emulsion and the external phases, so the proton gradient and the driving force increases as the pH of external phase increases [6]. These explain why the reading of extraction efficiency at pH 7 and 9 for copper were unusually higher than the other pH, which also means that acidic solution was preferred to prevent any possibility of precipitation occurring. Precipitation is necessarily avoided since the usage of acidic carrier, D2EHPA as the carrier in this process demands the metal to be in the form of free Cd^{2+} or Cu^{2+} cationic species to make it extractable by the acidic cation-exchange carrier [19]. Hence, the efficiency reading for pH 9 was considered invalid and pH 4 was chosen as the most effective pH for copper removal since 92.72% of copper was removed at this pH. The pH 4 was used for the next study as the best pH for copper and cadmium extraction efficiency.

The pH of the external phase has a profound effect on the extraction behavior [21] since solute removal within ELM system was generally governed by external phase pH. The formation of solute-carrier complex in the interface of external and membrane phase was highly influenced by the pH of external phase because the complex will only be built at suitable pH in which they can then diffuse effectively through membrane phase towards internal phase [16]. As can be seen, extraction process for both cadmium and copper was considered the best at acidic pH of 4, but further increase of pH led to substantial decrease of extraction efficiency. The decrease of extraction efficiency by the increase of external phase pH might also be driven by emulsion swelling phenomenon where it involved transport of water from external phase towards internal phase, causing membrane leakage and resulted to the release of entrapped metal back to external phase [16]. Emulsion breakage therefore, caused the extraction efficiency to decrease from the release of entrapped metal. On the other hand, the increase of external phase pH denotes the membrane rupture which resulted the internal phase to spill out into the external phase [22].

B. Effect of time and stirring speed on extraction efficiency

To analyze the performance of counter-rotating TCC for cadmium and copper extraction, the effect of extraction time and rotational speed on extraction efficiency were investigated and data collected are shown in Figure 5 and 6. For this study, rotational speed of the inner cylinder was remained constant at 40 rpm, while the rotational speed of the outer cylinder was varied from 0 to 600 rpm and the extraction process was done at varying time from 3 to 15 minutes. Theoretically, the use of Taylor-Couette Column (TCC) in copper and cadmium extraction was supposedly to enhance the extraction capacity, since the extraction can occur along the cylinder which also increases the contact area. Other than that, shorter time for extraction process can be expected by utilizing this system [9].

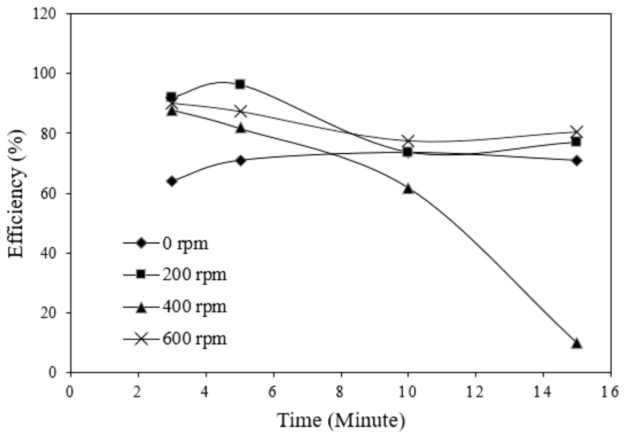

Figure 5: Effect of time and rotational speed of outer cylinder on copper extraction efficiency using TCC (surfactant concentration = 4 wt%; carrier concentration = 4 wt%; external phase pH = 4; rotational speed of inner cylinder = 40 rpm).

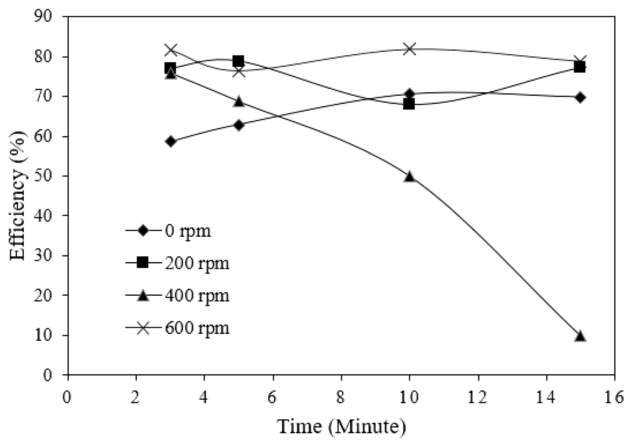

Figure 6: Effect of time and rotational speed of outer cylinder on cadmium extraction efficiency using TCC (surfactant concentration = 4 wt%; carrier concentration = 4 wt%; external phase pH = 4; rotational speed of inner cylinder = 40 rpm).

As can be seen from the figures, the highest extraction efficiency obtained for copper was 96.38% at 5 minutes with 200 rpm of stirring speed, while cadmium recorded 81.59% of extraction efficiency at 3 minutes with 600 rpm. Both Figure 5 and 6 showed that extraction process in TCC with the highest rotational speed of 600 rpm can result to the highest extraction efficiency of 81% as fast as 3 minutes. The extraction efficiency continued to increase as it reached 5 minutes, but started to decrease and plateau at times longer than that. The data obtained is in agreement with Zaulkiflee, et al. [10] and Raja Sulaiman, et al. [23] who also stated that the extraction time in ELM system was very rapid as the reaction kinetic occurred in a brief time. Normally, longer residence time enhances extraction efficiency since more solute will be extracted from external solution due to the increase of total mass transfer area of emulsion and external phase.

Other than that, since both graphs showed that high extraction efficiency were obtained at rotational speed of 600 rpm, it can be concluded that stirring speed directly influence extraction behavior which means the extraction efficiency was enhanced as the rotational speed increased [10]. The results can be basically justified that accelerating the rotational speed can lead to the decreasing of mass transfer resistance which also improved the external mass transfer coefficient and therefore, more metals were extracted into emulsion [24]. Low stirring speed on the other hand, resulted in the formation of large emulsion globules which thereby increased the thickness of membrane layer. The low stirring speed resultantly did not enhance the extraction process since large emulsion globule caused by the high thickness of membrane layer reduced the interfacial area for mass transfer. Emulsion with high viscosity could also affect the extraction efficiency by causing the formation of large emulsion droplets during dispersion, which resulted to lower interfacial area for mass transfer [5].

Generally, the extraction process should occur in thin liquid layer with tiny emulsions so that it could offer high transfer area. Once the membrane phase diffused into the internal phase, it will react with the carrier and supposedly not reversible to be diffused back to the external phase due to the insolubility of the complex [24]. Globule size distribution was influenced by stirring speed where higher speed led to the formation of minute size globules. Hence, increasing the interfacial area between external phase and the membrane phase by increasing the stirring speed will results to an increase in the rates of mass transfer which will then increase the extraction efficiency as can be seen in both figures where the efficiencies were mostly higher at stirring speed of 600 rpm compared to the other speeds. However, too high stirring speed can also cause side effects like more swelling and globule rupture [10].

Figure 6 showed that as the rotational speed of TCC outer cylinder increased from 0 to 600 rpm, the cadmium in external phase is extracted quicker, while lower rotational speed needed longer extraction time. This condition might be the result of decreasing boundary layer thickness for mass transfer at the outer interface by enhancing of mixing intensity. Mortaheb, et al. [7] also stated that the rise in overall mass transfer rate is much higher than the rise of the mixing intensity which can be associated to the incline in mass transfer interfacial area due to the globules size reduction. Nevertheless, there is possibility that the emulsion might be ruptured if subjected to higher mixing intensities.

The penetration of external phase into emulsion globule resulted to emulsion swelling which then increased the volume of emulsion during process. This scenario disrupted the extraction rate for diluting the internal phase and the concentrated solute in internal phase. On another notes, membrane breakage was related to the spill out of internal phase into external phase, resulted to the loss of entrapped solute and internal phase agent. The concentration gradient was hence decreased, leads to the depletion of mass transfer ability. The back diffusion of entrapped solute enhances the solute concentration which therefore decreases the extraction efficiency [9]. This also explains the drastic drop of extraction efficiency when subjected to 400 rpm rotational speed for 15 minutes and the almost constant extraction efficiency after 10 minutes time at 0, 200 and 600 rpm of rotational speed meaning that longer time will not increase the efficiency if the speed was high enough. The sudden drop of extraction efficiency at 400 rpm was in agreement with Othman, et al. [25]. Thus, shorter time was preferred for system done in higher rotational speed because the extraction time can be shortened by increasing the rotational speed.

Basically, all parameters studied for rotational speed of the two counter-rotating cylinders offered turbulent-based flow pattern which it usually will form high fluid mixing along the cell to provide a more efficient extraction process. In another words, the increasing outer cylinder rotational speed while fixing the inner cylinder rotation at a specific speed, the flow regimes converted from turbulent Taylor vortices to featureless turbulent regimes. This was also because the rise of the outer cylinder rotational speed that provided high mixing activity during the process resulted to the cadmium extraction rate improvement as can be seen in Figure 6 [9, 10]. The rotational speed of two counter-rotating cylinder that produced turbulent-based flow pattern usually provided high fluid mixing along the cylinder that can also result to an improvised extraction efficiency [10].

Based on the data plotted in Figure 5 and 6, it is basically proven that TCC offers higher extraction efficiency in relatively shorter contact time compared to conventional stirrer. Regardless of what kind of metal exhibits in the external solution that needs to be removed, extraction efficiency was not only considerably influenced by the emulsion composition but also by the configuration of TCC. Instead of utilizing single inner cylinder rotation, employing a two independently counter-rotating cylinders of TCC that had been used in this study managed to reduce energy loss along the gap, while was able to produce complex flow pattern and facilitated mass transfer in ELM process.

IV. CONCLUSION

Emulsion liquid membrane (ELM) employing Taylor-Couette Column (TCC) is a promising technique for heavy metal removal from waste water, specifically copper and cadmium. Experiments done showed that the capabilities of ELM for cadmium and copper extraction is substantially dependent on a number of operating conditions which some that had been studied in this work are pH, rotational speed and extraction time. From the data recorded, pH 4 was proved as the most suitable pH for copper and cadmium removal as the extraction efficiency for both metals were 92.72% and 81.29%, respectively. The pH for external phase for metal removal should be in acidic to avoid precipitation formed by the reaction of NaOH and metal compounds. Other than that, the rotational speed and extraction time that recorded the highest efficiency for copper were 200 rpm at 5 minutes with 96.38%, while for cadmium, the highest efficiency recorded was at 600 rpm in 3 minutes with 81.59%. It can be concluded that higher rotational speed needed shorter extraction time and copper ions showed higher selectivity compared to cadmium in TCC system.

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